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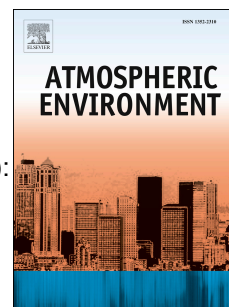
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Anthropogenic non-methane volatile hydrocarbons at Mt. Cimone (2165 m a.s.l, Italy): impact of sources and transport on atmospheric composition.

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Abstract

To advance our understanding of the factors that affect pollution in mountainous areas, long-term, high frequency measurements of thirteen Non Methane Volatile Organic Compounds (NMVOCs) have been carried out at the atmospheric observatory on the top of Mt. Cimone (2165 m asl), whose location is ideal for sampling both aged air masses representing the regional background and polluted air masses coming from nearby sources of anthropogenic pollution.

An analysis of the NMVOC time series available at Mt. Cimone during 2010 to 2014 was used to examine the influence of transport processes on NMVOC atmospheric composition and to derive information on the emission sources. We performed a multifactor principal component analysis whose results allowed us to identify the source categories emitting the NMVOCs measured at Mt. Cimone as well as to assess transport ranges in winter and summer. Aged air masses, due to long-range transport and related to vehicular traffic exhaust emissions accounted for 78% of the NMVOC variability in winter and 62% in summer, whereas evaporative emissions, likely to be associated with fresh emissions from nearby sources, accounted for 12% of the NMVOC variability and 24% in winter and summer, respectively. Such results have been confirmed by a further analysis in which the NMVOC variability as a function of their atmospheric lifetimes has been evaluated. The ratios of alkane isomers potentially provides a metric to investigate seasonal changes in NMVOCs composition and in the emission fields of butanes and pentanes, suggesting that during the summer the butanes are originating mainly from the European domain and that for pentanes non-anthropogenic sources may be contributing to the measured concentrations.

Keywords: Volatile Organic Compounds, Anthropogenic emissions, Emission patterns, Photochemical oxidation, Principal Component Analysis

1 Introduction

Non-methane volatile organic compounds (NMVOCs) are ubiquitous trace gases playing a crucial role in atmospheric chemistry as precursors of tropospheric ozone and of secondary organic aerosol (SOA). On the global scale the dominant sources of NMVOCs are biogenic (mainly forests) (Kansal, 2009). However, non-biogenic sources, such as biomass burning, and purely anthropogenic sources such as vehicular exhaust emissions, solvent use and the use and distribution of petroleum products are particularly relevant in the more densely populated areas of the northern hemisphere.

Once emitted into the atmosphere, NMVOCs react with the atmospheric oxidant hydroxyl radical (OH), ozone (O₃) and nitrate radical (NO₃) (Atkinson and Arey, 2003); the atmospheric lifetime of individual compounds depends on the rate of such reactions taking place during transport from the source regions, and determines the range of transport times (Heard, 2007). Longer-lived compounds can be transported on a synoptic-scale, advected by large-scale winds. Short-lived species originating from sources within a regional domain, are dispersed by small-scale circulation systems such as mountain-valley winds or deep convection and can occasionally be transported by the fast winds into the free troposphere on the synoptic and hemispheric scale (Monks et al., 2009; Purvis et al., 2003). With respect to the long-range transport of pollutants imported to Europe, the most important synoptic scale features are the mid-latitude cyclones that form above eastern North America, following the North Atlantic storm track to Europe. These systems export large quantities of trace gases from the boundary layer of the North American east coast (Cooper et al., 2002; Stohl et al., 2002) into the European free troposphere. Investigating the effect of the interaction between transport processes and atmospheric oxidation on the mixing ratios of NMVOCs measured at a given receptor site is useful for identifying sources and verifying their impact on the oxidation capacity of the atmosphere.

Mixing ratio patterns of anthropogenic NMVOCs correspond to specific and well characterised emission sources, as supported by a number of data-sets available for several urban environments where most sources are located (Derwent et al., 2000; Parrish et al., 1998). During transport, NMVOC patterns can be modified by progressively larger dilution and photochemical removal.

For compounds with lifetimes up to one week, such as butane and pentane isomers, their ratios have been shown to be a robust metric to assess to what extent the transport on synoptic scales influences the NMVOC mixing ratios measured at the receptor. Many studies have reported that butane and pentane isomers are emitted in a broadly constant ratio by their sources; thus, given their different reactivity, their ambient ratios are useful for investigating sources and atmospheric oxidation processes (Helmig et al., 2014; Yates et al., 2010). There are several factors driving the alkane isomer pair ratios: emission categories/ratios at the injection point, atmospheric dispersion and OH photochemical removal. Emission sources of n-butane and i-butane include combustion, evaporation of fossil fuels and the production and refining of petroleum, all of which emit varying ratios of n- and i-butane (Lee et al., 2006). The OH reaction

rate constants of the isomeric pairs *i*- and *n*-butane are very similar; consequently, the ratio of these two compounds is not expected to change during transport (Helmig et al., 2008). Previous studies (Derwent et al., 2000; Parrish et al., 1998) concluded that close to emission sources the *i*-/*n*-butane mean ratio is maintained nearly constant, ranging from 0.4 to 0.6. In fact, emissions from various butane sources in a given region mix rapidly in comparison to the butane isomer lifetimes and to the average mesoscale transport times to the receptor (Lee et al., 2006). Seasonality in the *n*-/*i*-pentane isomer ratio has been used to assess the role of the nitrate radical in clean air masses sampled in the free troposphere compared to those observed in recently polluted air (Penkett et al., 2007).

Studies conducted at a receptor like Mt. Cimone (CMN) are particularly significant because of the proximity of the site to the Po basin, a mega-city like environment in Northern Italy, one of the most important source regions in Europe for anthropogenic atmospheric pollutants. CMN represents a strategic site for investigating the effects of regional and long-range transport of polluted air masses over the free troposphere (Carbone et al., 2014), its location being ideal for sampling air masses with different origin, from the cleaner air masses representing the regional background to the more polluted air masses coming from the Po basin.

Long-term, high-frequency and high-precision measurements of ethyne, C_3 - C_7 alkanes, and C_6 - C_8 aromatics have been carried out at CMN since January 2010 as part of the ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network) EU infrastructure project, aimed at creating a European observation network for highly time-resolved NMVOC observations (Hoerger et al., 2015). NMVOC data from eleven sites across Europe (including data presented in this paper) contributing to ACTRIS are publicly available at ebas.nilu.no.

Time series data as well as the annual and seasonal variability of NMVOCs at CMN have been reported in a recent study by Lo Vullo et al. (2016), who found during the study period (January 2010 to December 2014) a decreasing trend for most of the investigated species, reflecting the effects of the implementation of air pollution policies in Europe. A clear seasonal variability was also been shown, characterised by small seasonal amplitudes for the shorter-lived species. Long term variability and seasonal cycles have been calculated after a characterisation of air masses on the basis of their different origin (clean vs polluted sectors). The characterisation was made using a statistical filtering technique (Giostra et al., 2011) allowing the distinction to be made between regional background (well-mixed) conditions and fresh emissions of pollutants above the background concentrations.

Lifetimes of the compounds considered in this study range from hours to weeks, corresponding to transport scales from local to intercontinental. Although it is well known that NMVOCs have significant and well characterised anthropogenic emission sources, the relative importance of the various sources is still poorly understood and under debate (Salameh et al., 2016). Each emission source has a distinctive speciation profile and it may have a different, site-dependent impact on regional and global air quality and

climate. Therefore, in order to assess the source-receptor relationships of NMVOCs detected at CMN and in order to investigate atmospheric transport processes and chemical conversions occurring en route across different spatial scales, we analysed the five-year time series available at CMN using different approaches: i) we used Principal Component Analysis (PCA) followed by Varimax rotation (Guo et al., 2006) as an exploratory tool to identify the major NMVOC emission source categories and to select statistically independent source tracers; ii) the relationship between the variability of the single NMVOC mixing ratios and their reactivity with OH radicals has been used to investigate the role of atmospheric mixing and chemistry in winter and summer; iii) the seasonal variation of butane and pentane isomer ratios at CMN both during pollution events and in well-mixed conditions has been used to assess the influence of transport on diurnal and night-time chemistry, respectively.

2 Material and Methods

2.1 Analytical method

Long-term observations of thirteen NMVOCs are conducted at the Italian Climate Observatory “O.Vittori” (44°12' N, 10°42'E), a global GAW-WMO (Global Atmospheric Watch of the World Meteorological Organisation) site located on the top of Mt Cimone at 2165 m a.s.l., the highest peak of the Italian Northern Apennines, facing the highly polluted Po valley. The measurement site can generally be considered representative of the background conditions of the Southern European free troposphere. Details of the station characteristics are given in Carbone et al. (2014). CMN is also an affiliated AGAGE (Advanced Global Atmospheric Gases Experiment) station measuring the most important ozone depleting compounds (Graziosi et al., 2015; Maione et al., 2013, 2014) and climate altering gases, see e.g. Stohl et al. (2009).

NMVOCs in ambient air are analysed via gas chromatography–mass spectrometry (GC–MS) with the MS detector operating in selective ion mode (SIM). The GC–MS Agilent 6850–5975 instrument has been equipped with an auto-sampling/pre-concentration device (Markes International, UNITY2-Air Server2) to enrich the NMVOCs on a focussing trap cooled to -30°C. A Nafion drier tube is used to reduce the sample moisture both in real air and in the working standard. Details of the analytical procedure are reported in Maione et al., (2013). Annual mean percent relative standard deviations (%RSD) are evaluated from the repeated working standard measurements (RSD over 1 year). Absolute total uncertainty (TU, coverage factor=2), in ppt, is calculated including the certified uncertainty in the standard gas mixing ratio that propagates on the calibration chain. Limits of detection (LODs), (Signal to Noise, S/N>3) and limits of quantitation, LOQs (S/N>10) have been indirectly estimated on the chromatogram of the working standard run (Lo Vullo et al., 2016).

Ambient air aliquots are sampled every two hours and each sample takes about 26 minutes to collect. The sample analyses are bracketed by working standard analyses, in order to detect and correct for short-term instrumental drift. These working standards are air samples that are pumped during relatively clean-background conditions into 35-l electro-polished stainless steel canisters (Essex Cryogenics, Missouri, USA) using a modified oil-free compressor (SA-3 or SA-6Rix California, USA) up to ~60 bar. The working standards are calibrated against a primary reference standard prepared by NPL (National Physical Laboratory, Teddington, UK). The gas mixture contains thirty hydrocarbons with certified concentration around 4 ppb; absolute concentrations are propagated to a lower concentration standard in air, that is used to calibrate the working standard. The GC-MS system is fully automated via the Linux-based chromatography software (GCWerks, www.gcwerks.com) adopted by the AGAGE programme.

CO is measured with a Gas Chromatograph (GC) equipped with a Flame Ionization Detector (GC-FID). The instrument has been running continuously since January 2008. Air samples are flushed continuously from the main common inlet at the station through a 10 ml stainless steel sampling loop, mounted on a 10 way ViciValco Valve configured for the loop sampling with backflush of the pre-column. Every 15 min, the valve

is actuated to inject the air sample into the GC for the separation in the dual column system (2 x 3 feet long, 1/8" OD columns packed with Mol. Sieve 5A -main column- and Unibeads 1S -precolumn) and backflush of the undesired heavier compounds to vent; then the CO peak is diverted to the Hot Nickel Oxide converter (methanizer) to reduce CO to Methane prior the detection on the FID. Each analysis sample is alternated with a calibration sample (real air working standards representative for ambient air mixing ratios for the Northern Hemispheric troposphere). The working standards were prepared at the station pumping real air during clean air conditions in Luxfer passivated Aluminum cylinder in dry condition and calibrated regularly against a batch of 5 NOAA cylinders on the WMO-X2014 scale. This guarantees a continuous check of the detector calibration (Novelli et al., 1999) with a precision, in term of daily relative standard deviation over repeated analysis of the working standards (48 runs) of 0.6 %.

2.2 Multivariate analysis: Principal component analysis (PCA)

The Principal Component Analysis (PCA) receptor model was used to study the impact of relevant sources of NMVOCs at CMN. PCA is a well-established tool for analysing structure in multivariate environmental data sets (Borbon et al., 2003). The main objective of PCA is to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables, called principal components (PCs) (Belis et al., 2013). The statistical analysis of CMN data was performed by using the SPSS statistical software package. The number of extracted PCs corresponds to the number of source categories. Factor loadings indicate the correlations of each pollutant species with each factor and determine the more representative compounds in each factor.

Since skewness and the magnitude of the variables can influence the resulting PCs, before using the PCA we have applied a log transformation to the dataset. Then we have proceeded to data standardization so that the variables have mean 0 and variance 1 (Guo et al., 2004).

The multivariate method is achieved by orthogonal transformation with Varimax rotation and the retention of principal components whose eigenvalues are greater than one. Only the principal components that explained more than 5% of total variance of the data set were used as factors.

Finally in this study, a listwise technique (Widaman, 2006) was adopted to handle missing data. Values below the quantification limit (LOQ) are not present in our record and the missing data are due to instrument failures, troubles to the sampling facility at the station (including local contamination) or instrument maintenance (including calibrations, comparisons, round robins).

The individual samples have been checked and those with unusually high or low concentrations have been identified as outliers.

2.3 Conditional probability function

The conditional probability function (CPF) is a common tool used to provide directional information concerning major sources (Uria-Tellaetxe and Carslaw, 2014). CPF is defined as $CPF = m_{\theta}/n_{\theta}$, where m_{θ} is the number of samples in the wind sector θ with mixing ratios that exceed the threshold criterion, and n_{θ} is the total number of samples in the same wind sector, providing the probability that in a specific wind sector the mixing ratio of a compound is greater than the chosen threshold. The sources are likely to be located based on the wind directions that have high conditional probability values.

3 Results and discussion

Table 1 reports the average winter (December, January, February) and summer (June, July, August) mole fractions and ranges of NMVOCs and carbon monoxide (CO) measured at CMN, averaged over the study period (January 2010 to December 2014).

The mole fractions of NMVOCs change seasonally, with winter maxima and summer minima. The

Table 1: Annual NMVOC (part per trillion, ppt) and CO (part per billion, ppb) statistic for the whole data set at CMN (2010-2014). N is the number of samples.

Species	Winter (DJF)			Summer (JJA)		
	Mean	Range	N	Mean	Range	N
CO	139	54-442	1902	115	58-318	2927
Ethyne	268	59-1875	3009	70	8-250	3261
Propane	634	81-2114	3007	168	26-1405	3327
Benzene	134	16-1105	3391	42	12-114	2996
i-butane	119	6-552	3472	33	2-526	3331
n-butane	223	14-793	3542	52	5-542	3283
i-pentane	74	2-823	3540	39	1-382	3265
n-pentane	60	3-344	3426	24	3-333	3340
n-hexane	17	0.1-137	3418	4	0.2-35	3069
Toluene	58	0.1-794	3391	30	3-315	3291
n-heptane	7	0.01-656	3520	2	0.3-447	3045
Ethyl-benzene	12	0.2-99	3401	9	1-44	3273
o-xylene	10	0.1-337	3377	6	0.5-53	3084
m,p-xylene	32	0.1-362	3340	15	1-150	3078

seasonality in composition can be due to dilution by atmospheric mixing, photochemical processes, changes in meteorological patterns or emission patterns. However, inter-seasonal changes in NMVOC composition are a site-specific feature, essentially related to the location of the measurement site.

Figure 1 reports the NMVOC time series at CMN during January 2010-December 2014. As shown by Lo Vullo et al. (2016), a more pronounced seasonal cycle is exhibited by the longer-lived compounds, i.e. ethyne, C3-C5 alkanes, benzene and toluene.

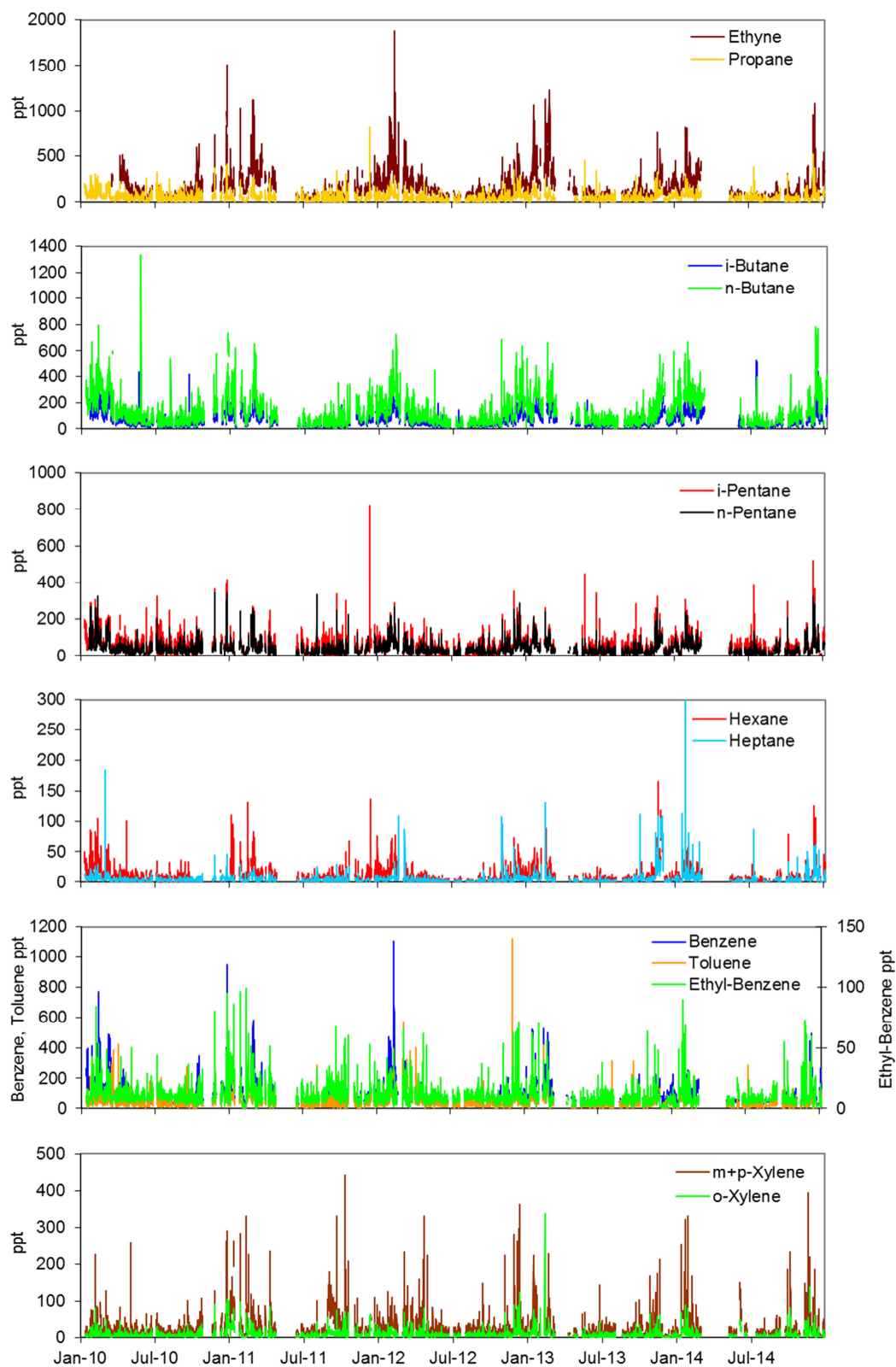


Figure 1: Time series of NMVOCs at Mt. Cimone from January 2010 to December 2014. Mole fractions are given in ppt.

3.1 Principal component analysis of NMVCOs at CMN

Carbon monoxide (CO) was included in this analysis as a long-lived combustion tracer. As suggested by Leuchner et al. (2015) and Lanz et al. (2009), the resolved profiles at remote sites should be read as “aged profile”, reflecting both source patterns and transport processes.

We adopted Kaiser’s criteria to determine the appropriate number of components (i.e. only factors with eigenvalues ≥ 1 were retained). The statistical results for the winter (DJF) and summer (JJA) seasons are shown in Table 2, where only compounds with factor loadings ≥ 0.50 are reported.

After applying the PCA to the wintertime data, two components were extracted. The first factor (WF1) explained 78% of the total variance and the second factor (WF2) accounted for 12%. Ethyne, propane, butanes and benzene are represented especially in WF1. Toluene and pentanes are related to both factors while ethyl-benzene and xylenes contribute mostly to WF2.

Table 2: Seasonal PC analysis of NMVOCs and CO at Mt Cimone. Extraction Method: principal component analysis. Rotation Method: Varimax with Kaiser normalization. Only factor loadings ≥ 0.50 are listed.

	Winter (DJF)		Summer (JJA)		
	WF1	WF2	SF1	SF2	SF3
CO	0.91		0.90		
Ethyne	0.91		0.86		
Propane	0.87		0.78	0.50	
Benzene	0.91		0.83		
i-butane	0.87		0.63	0.67	
n-butane	0.83		0.62	0.72	
i-pentane	0.77	0.54		0.83	
n-pentane	0.81	0.50		0.81	
n-hexane	0.86			0.86	
Toluene	0.61	0.72		0.72	
Ethyl-benzene		0.86		0.51	0.75
o-xylene		0.94			0.95
m+p-xylene		0.97			0.97

Factor WF1: the high factor loading for CO and the lack of shorter-lived compounds suggest that this factor represents aged air masses, due to long-range transport. This factor includes i) ethyne, emitted mainly by automobile exhausts (Lee et al., 2006); ii) C3-C5 alkanes, related to gasoline evaporation and generation of

Liquified Petroleum Gas-LPG (Barletta et al., 2005); iii) toluene and n-hexane, related to solvent evaporation (Moschonas and Glavas, 2000), as well as to vehicular exhausts.

Factor WF2: short-lived species are dominant in factor WF2. High factor loadings were found for toluene, ethyl-benzene, xylenes (TEXs) and pentanes. The low factor loading for CO suggests that this factor is not related to combustive aged air masses, but might be associated with fresher emissions. Since TEXs are mainly used as solvents in the paint industry, species in WF2 could be associated to industrial solvent evaporation. The lower factor loading of pentanes, known to be tracers of gasoline evaporation, suggests that gasoline evaporation is contributing to WF2 but to a lesser extent.

For the summer data, the PCA identifies three components: SF1, accounting for 62% of total variance and SF2 and SF3 explaining 16 and 8% of the total variance, respectively.

Factor SF1: High factor loadings were observed for CO, propane, ethyne and benzene, which are the least reactive compounds, suggesting that this factor describes, as for factor WF1, air masses that underwent long-range transport.

Factors SF2 and SF3: these factors are not correlated with CO and are representative of emissions from medium-range transport and local sources. Pentanes, hexane and butanes, related to fuel evaporation, are the main components of SF2. The solvents ethyl-benzene and xylenes are strongly related to SF3.

In conclusion, this analysis suggests a characterisation of the contribution at CMN of NMVOC source categories, highlighting season-specific patterns: in wintertime the NMVOC variance is mainly due to long-range transport, with WF1 factor accounting for the 78% of total variance, the homologous summer factor SF1 contribution decreases to 62%.

3.2 Variability-lifetime relationship

The relationship between the variability of NMVOCs and their lifetimes has been used to investigate the potential impact of local emissions and the relative influence of mixing and chemistry (Jobson et al., 1998, 1999). Here we use the variability-lifetime relationship to further investigate the degree of influence of local emissions on the NMVOC mole fractions measured at the receptor, both in summer and winter. Jobson et al. (1998) first proposed for a set of NMVOCs, the relationship $\sigma_{\ln X} = A\tau^{-b}$, where $\sigma_{\ln X}$ is the standard deviation of the natural logarithm of the mixing ratio X of a given compound, τ_{OH} is its estimated atmospheric lifetime with respect to reaction with OH, and A and b are empirical parameters. A higher variability is expected for reactive compounds, which are removed from the atmosphere more rapidly than long-lived species.

Figure 2 shows the variability-lifetime relationship for NMVOCs measured at CMN in winter (solid line) and in summer (dotted line), with the respective empirical fitting parameters A and b .

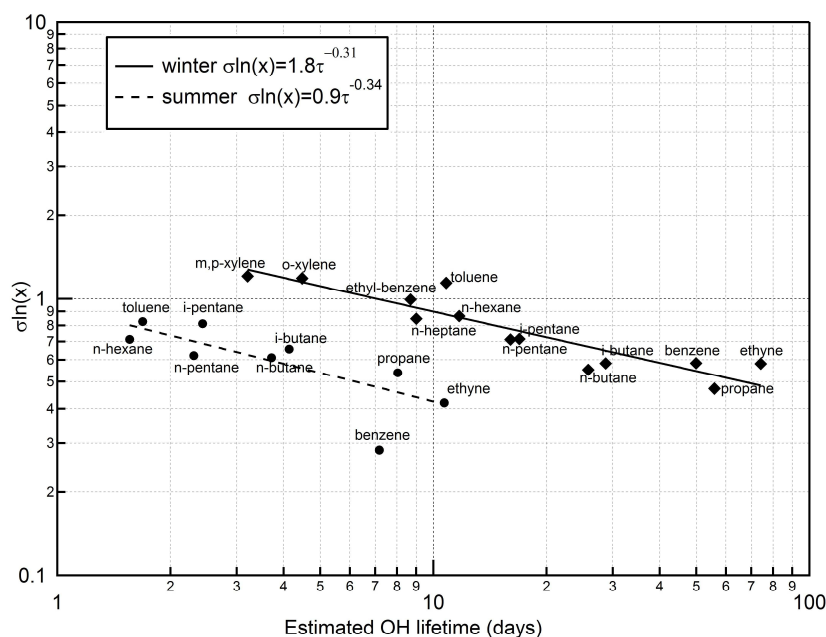


Figure 2: Standard deviation of the natural logarithm of NMVOC mixing ratios ($\sigma_{\ln X}$) in summer (circles) and winter (diamonds). NMVOC lifetimes, $\tau = 1/K_{OH} \times [OH]$, are estimated using an OH concentration $\approx 1.32 \times 10^6$ molecules cm^{-3} in summer and $\approx 1.19 \times 10^5$ molecules cm^{-3} in winter (Mészáros et al., 2004). The rate coefficients are taken at 298 K from Atkinson and Arey (2003).

The b factor essentially describes the influence of the emission sources (Jobson et al., 1998). Different studies have shown that b values close to 1 are found in stratospheric samples where the variability is driven by chemical loss only. On the contrary, in urban areas b values approach 0, reflecting the variability of local emission sources (Helmig et al., 2008). For remote tropospheric sites, where the influence of nearby sources is not significant, observations showed b values ranging between 0.28-0.56 (Karl et al., 2001).

The use of the relationship between variability and lifetimes is possible only when all the considered species are originating from the same source domain (Bartenbach et al., 2007). In order to comply with this condition, NMVOCs with lifetimes longer than 36 hours have been used for this analysis. The 36-h threshold has been chosen as an estimate of the timescale of transport from sources in the whole European domain. During the winter, this condition is satisfied by all the compounds considered in this study whereas in the summer, compounds like n-heptane, ethyl-benzene and the xylenes isomers fall in the lifetime range < 36 hours. Hence, these more reactive compounds have not been included in the summer analysis.

The b values obtained at CMN fall in the range 0.28-0.56 in both seasons, suggesting that NMVOC variability at the receptor is mainly due to long-range transport (photochemical ageing modulated by mixing), in agreement with the results obtained through the PCA, where WF1 and SF1 are the dominating factors. The A parameter is a proportionality constant and could represent a measure of the range of air mass ages in the data set, which is determined by the different travel times of the compounds from their emission source to the receptor (Williams et al., 2000). For air masses with a narrow age range (i.e. nearby sources affecting the receptor), A values are expected to be lower than those found when aged air masses reach the receptor. Even if, differently than the b parameter, A is affected by the chosen OH concentration values, relative A values can provide interesting insights on air mass age range. A values at CMN range from 0.9 to 1.8 in summer and winter, respectively. These relatively low A values provide an indication that at CMN air masses with a small age range are also sampled (Williams et al., 2000), as also shown by factors WF2, SF2 and SF3 in the PCA.

3.3 Butanes and pentanes ratios

As reported by Yates et al. (2010) ratios of isomeric pairs can be modified during transport to the receptor due both to oxidation processes or to the fact that different emission sources are sampled. Therefore, in order to evaluate the role of transport and photochemistry we analysed the butane and pentane isomers ratios and compared our results with previous studies, identifying different behaviours in polluted and clean conditions.

In Figure 3 the butane and pentane isomer ratio plots are reported. The i-/n-butane scatter plot (Fig 3a) shows fairly constant and high correlation values throughout the year, with slope values of 0.57 ($R^2 = 0.95$) and 0.65 ($R^2 = 0.91$), for winter and summer, respectively. Spring and autumn values, not shown, were 0.56 ($R^2 = 0.95$) and 0.51 ($R^2 = 0.90$), respectively. The measured overall i-butane versus n-butane ratio is 0.56, showing how the typical ratio at the emission source (0.4-0.6) (Derwent et al., 2000; Parrish et al., 1998) does not significantly change at CMN.

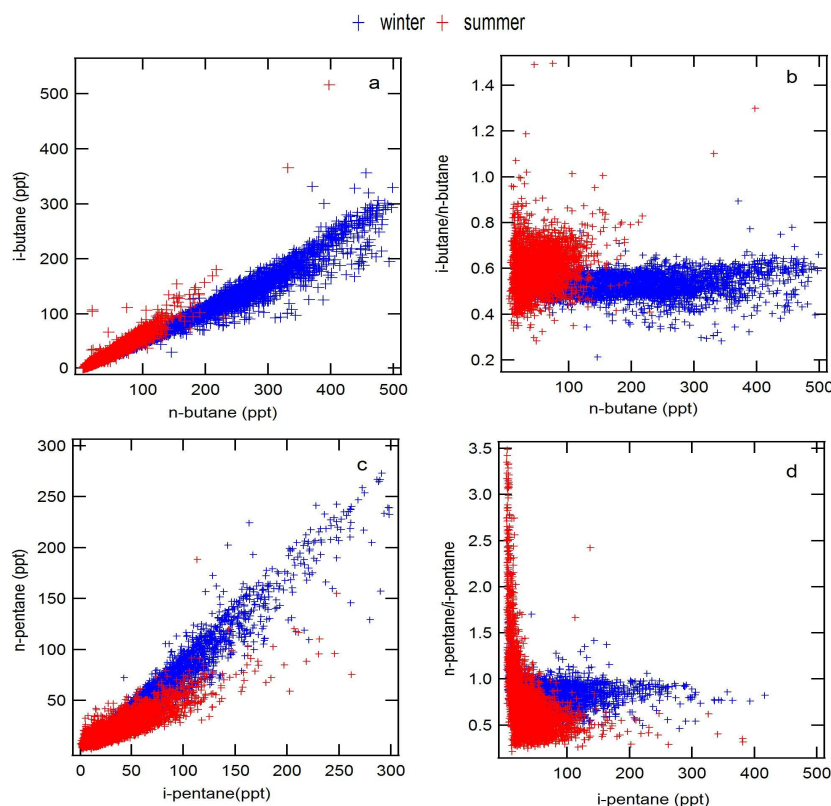


Figure 3: Seasonal variation of butane and pentane isomers during 2010-2014. (a) [i-butane] versus [n-butane]; (b) [i-butane]/[n-butane] versus [n-butane]; (c) [n-pentane] versus [i-pentane]; (d) [n-pentane]/[i-pentane] versus [i-pentane]

Figure 3b reports the [i-butane]/[n-butane] ratio plotted against [n-butane]. Our results show that during the winter season, the i-butane/n-butane ratios are quite independent from n-butane mole fractions indicating a not significant impact of photochemical processing on the i-/n-butane ratio. During summertime we observe a general increase of this ratio and related variability, with the standard deviation σ going from 0.05 in winter to 0.16 in summer. This can be explained by OH chemistry: if the evolution of i-/n-butane ratio is driven by OH oxidation, as the transport time increases a rise in i-/n-butane ratio would be expected, due to the lower n-butane OH reaction rate constant ($2.36 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) compared to i-butane ($2.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

Assuming an OH average European summer concentration of $1.32 \times 10^6 \text{ molecules cm}^{-3}$ (Mészáros et al., 2004) and assuming that the average butane winter ratio is representative of the ratio at the emission source, equation (1) can be used to derive a transport time t if the photochemistry only is taken into account:

$$t = \left\{ \ln \left(\frac{i-but}{n-but} \right)_{source} - \ln \left(\frac{i-but}{n-but} \right)_{receptor} \right\} / \left\{ (k_{OH|i-but} - k_{OH|n-but}) \cdot [OH] \right\} \quad (1)$$

where $(i\text{-}n\text{-}but)_{source}$ is the average *i*-/*n*-butane winter ratio, $(i\text{-}n\text{-}but)_{receptor}$ is the instantaneous *i*-/*n*-butane ratio at the receptor. k_{OH} is the OH reaction constant and $[OH]$ is the hydroxyl radical concentration. In Figure 4 is reported the normalised Probability Density Function (PDF) of the transport time t , from the source to the receptor, for the *i*-/*n*-butane summer ratio.

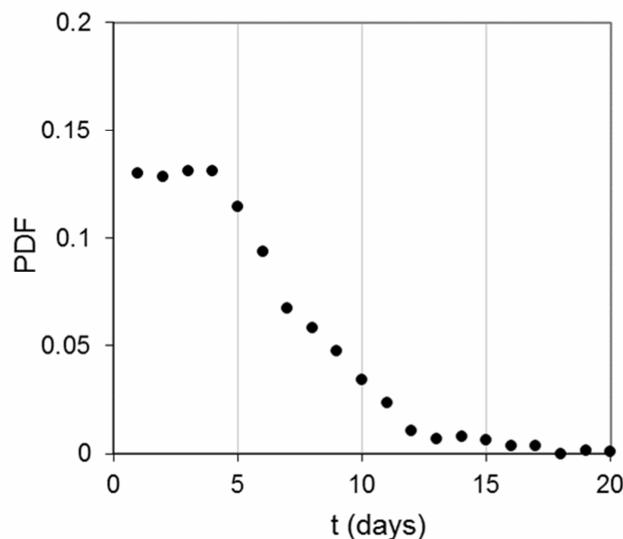


Figure 4. Normalised Probability Density Function (PDF) of the transport time t for the summer *i*-/*n*-butane ratio.

The plot shows how most of the data have a transport time shorter than four-five days. This time scale corresponds to the typical synoptic scale, suggesting that NMVOCs measured at CMN are mainly originated from the European domain.

Table 3 reports the average *i*-/*n*-butane ratio at CMN compared with two other European mountain GAW stations (data available at the World Data Centre for Greenhouse Gases, <http://ds.data.jma.go.jp/gmd/wdcgg/>). All sites show comparable values of butane ratios, both in wintertime and in summertime indicating a similar pattern in transport processes to these nearby sites.

Figure 3c shows the correlation plot between *n*- and *i*-pentane throughout the year, with ratio values of 0.82 ($R^2 = 0.94$) and 0.45 ($R^2 = 0.70$) in winter and summer, respectively. Spring and autumn values (not shown) were 0.71 ($R^2 = 0.80$) and 0.71 ($R^2 = 0.90$). The overall *n*-/*i*-pentane ratio observed at CMN during the study period is 0.74 ($R^2 = 0.90$), this is in good agreement with data reported in the GAW remote sites of Mace Head in Ireland, 0.74 ($R^2 = 0.95$) (Yates et al., 2010) and Pallas in the subarctic region 0.74 ($R^2 = 0.96$) (Hellen et al., 2015). The CMN summer ratio (0.45) is roughly half the winter one (0.82). This is

consistent with the fact that when OH oxidation dominates, a decrease in the n-/i-pentane ratio with increasing transport time is expected, because of the slightly higher n-pentane OH reaction rate constant. Hoenpeissenberg presents a similar pattern, although the winter value is lower than that at CMN.

Table 3: Average ratio of alkanes isomers at three European remote mountain sites

Remote GAW Stations	Average i-butane/n-butane		Average n-pentane/i-pentane	
	Winter(DJF)	Summer (JJA)	Winter(DJF)	Summer (JJA)
CMN (IT)	0.57	0.65	0.82	0.45
Jungfraujoch (CH)	0.55	0.59	-	-
Hoenpeissenberg (DE)	0.59	0.68	0.60	0.50

As shown in figure 3d, at very low (below 20 ppt) levels of n-pentane, typical of aged air masses, we observe an increase in the n-/i-pentane ratio. This suggests the possible influence of the night-time oxidation of NMVOCs: as highlighted by Penkett et al. (2007), oxidation of NMVOCs by NO₃, the typical night time oxidant, would shift the n-/i- isomer ratio to higher values since the reaction of NO₃ with i-pentane is about twice as fast as that with n-pentane. However, considering a transport time of three days from urban areas to CMN, and that NO₃ is formed only during the night, the estimated NO₃ concentration needed to change the n-pentane/i-pentane ratio from 0.82 to 3.0 would be ca. 900 ppt, which is an unrealistic level. Measurements of nitrate radicals in night time continental boundary layers have reported much lower concentrations of NO₃, below 100 ppt (Yates et al., 2010).

Therefore, other sources should be considered. Figure 5 reports how n-/i-pentane ratios significantly depend on seasonality and on wind sectors. Enhanced n-/i-pentane ratios (≥ 1.5), occurring mainly during the summer and completely absent during the winter, appear to be preferentially linked to the transport of air masses from South Western sectors. This evidence supports the hypothesis that the variation in the n-/i-pentane ratio could be due to the influence of non-anthropogenic sources, such as biomass burning and oceanic sources that preferentially emit n-pentane (Helmig et al., 2008; 2014). The influence of fires occurring in the Mediterranean basin during the warm season on the atmospheric composition at CMN has been reported by Cristofanelli et al. (2013). In addition, this behaviour characterised by high n-pentane/i-pentane ration is not found in the other GAW mountain sites.

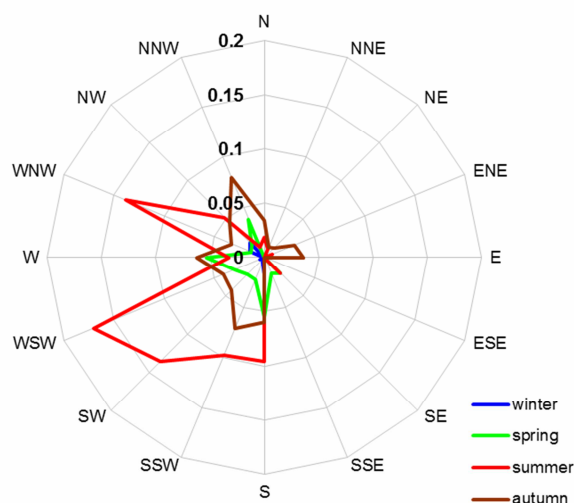


Figure 5: Conditional Probability Function plots of n-/i-pentane at Mt Cimone in different seasons.

Conclusions

There are multiple factors making the analysis of NMVOC time series a challenging task: the multiplicity of emission sources, dispersion en route to the receptor site and photochemical removal and oxidation processes that are functions of transport time and atmospheric composition. In spite of such complexity, the study of NMVOCs can be tackled using different approaches that can provide important insights into sources and processes occurring during transport. A receptor site that can be affected, depending on the various meteorological and climate conditions, both by regional (mesoscale) and remote (synoptic scale) sources has proven to be particularly interesting, notwithstanding the difficulty in the interpretation of results. In this study, we analysed five-year (January 2010 to December 2014) time series of NMVOCs at Mt. Cimone station. Principal Component Analysis results allowed us to identify the main emission source categories and two different seasonal transport patterns, with 78% of the wintertime NMVOC variability explained by long-range transport and 62% in the summer. Such findings are confirmed by the analysis of the relationship between variability and lifetime.

The i-/n-butane ratios suggest that the butane emission domain affecting CMN during the summer is mainly European. Ambient concentration ratios significantly different from those at sources can help in assessing the extent of the emission domain affecting CMN. For two isomers having an average lifetime of about 4 days and with a difference in lifetimes between the two isomers of only 10%, longer temporal scales would be needed (extra-European) in order to observe i/n-isomer ratio values significantly differing from those observed at the source regions. An increase in the n-/i-pentane ratio observed in aged air

masses (low i-pentane mole fractions) seems to be unrelated to oxidation by NO₃ but rather suggests the occurrence of non-anthropogenic sources.

In conclusion, this study allowed us to characterise the drivers of NMVOC atmospheric composition at a site located at the interface between the Mediterranean and continental Europe. Our results can provide important site-specific information for a better understanding of the formation at the regional scale of secondary pollutants relevant both for air quality and climate.

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571

Research highlights

NMVOC speciation profile is site-specific and so is its impact on air quality and climate

Vehicular traffic exhaust emissions are the prevailing source category in our study area

Different seasonal patterns are observed corresponding to different transport ranges